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1980

Kinetics and Mechanism for Reduction of Tetrachloro- and
Tetrabromoaurate(III) by Iodide.

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Running title: Reduction of Tetrahaloaurate(III)

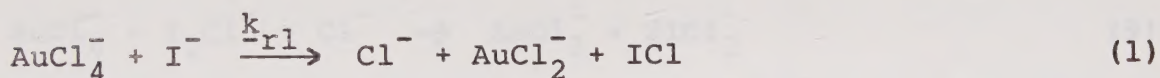


Reduction of tetrachloro- and tetrabromoaurate(III) to gold(I) by iodide in aqueous solution has been studied by stopped-flow spectrophotometry using either excess iodide or excess gold(III) complex. For excess iodide, there is one single reaction, whereas for excess gold(III), reduction takes place in two consecutive steps because rapid equilibria involving the polyhalide anions ICl_2^- and I_2Cl^- influence the kinetics. Reduction by iodide is faster than ligand substitution in both AuCl_4^- and AuBr_4^- , so there is no initial replacement of chloride or bromide by iodide prior to the reductive elimination. The mechanism is thus intermolecular, involving a direct attack on one of the halide ligands of the complex by iodide in the rate-determining step. The rate constants for reduction of AuCl_4^- and AuBr_4^- by iodide at 25.0°C are $(9 \pm 1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $(10 \pm 3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for a 1.00 M perchlorate medium.

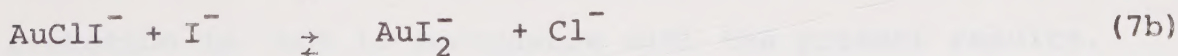
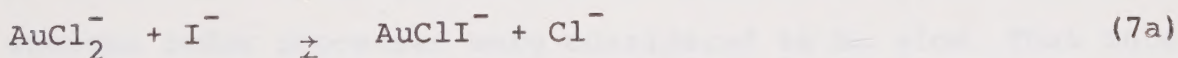
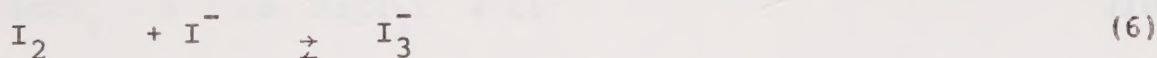
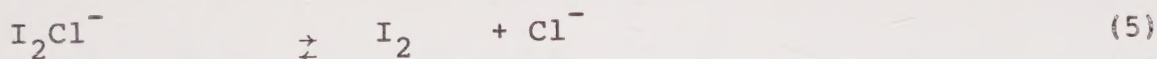
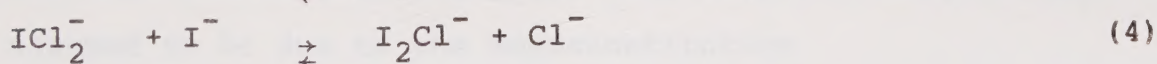
Introduction

Tetrachloro- and tetrabromoaurate(III) complexes are rapidly reduced to gold(I) complexes by iodide in aqueous solution.¹ The diiodoaurate(I), AuI_2^- , is well known.² Solid complexes containing I_4^- units have been prepared³ and the existence of AuI_4^- complexes in equilibrium with AuI_2^- and I_3^- in aqueous solutions saturated with iodine has been demonstrated. We here report a study of the reaction mechanism for reduction of AuCl_4^- and AuBr_4^- to gold(I) by iodide.

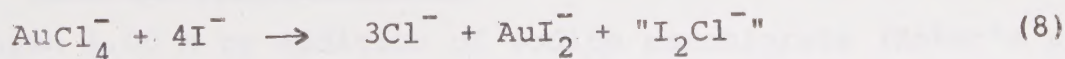
For excess iodide and in the presence of chloride (0.1 to 1 M; necessary to suppress aquation of AuCl_4^-) one pseudo first-order reaction is observed in the AuCl_4^- -iodide system. The kinetics can be interpreted in terms of a rate-determining reduction:



followed by a series of rapid equilibria:



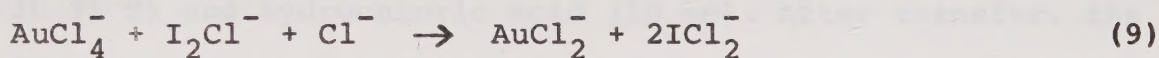
The over-all reaction for the experimental conditions used can be written



where " I_2Cl^- " stands for an equilibrium mixture of I_2Cl^- , I_2 and

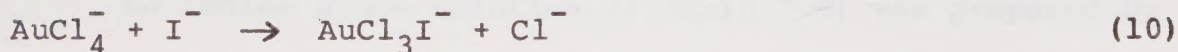
I_3^- . The distribution of these species is determined by the concentrations of free iodide and chloride according to reactions 4, 5 and 6. The chemistry of polyhalide anions has been reviewed. The equilibrium constants for reaction 4 to 6 are $K_2 = 90$ (this work), $K_3 = 3 \times 10^6 \text{ M}^{-1}$,⁷ $K_4 = K_3/2 = 1.5 \times 10^6$ (this work) $K_5 = 0.57 \text{ M}$ (this work and Ref. 5) and $K_6 = 710 \text{ M}^{-1}$.⁷

If instead excess tetrachloroaurate(III) is used, the kinetics is more complex. Two consecutive reactions in different time scales can be observed. The initial rapid step can be identified as a reduction of $AuCl_4^-$ by half of the amount of added iodide according to reaction 1, the products being mainly I_2Cl^- and I_2 . In the subsequent slower process, there is a further reduction of gold(III) according to



The experimental rate law for this latter reaction indicates a complicated mechanism.

One report on the kinetics for the $AuCl_4^-$ - iodide reaction has been published previously.⁸ The observed reaction was assumed to be due to the monosubstitution



whereas redox processes were considered to be slow. That interpretation is not in accordance with the present results.

Experimental Section

Chemicals and Solutions. All solutions had the ionic strength 1.00 M by addition of sodium perchlorate (Baker's p.a. recrystallized once) and perchloric acid (Baker's p.a.). Stock solutions of tetrachloro- and tetrabromoaurate(III) (2.5 mM)

were prepared from $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$; $x \approx 3$ (Degussa). To suppress hydrolysis, they also contained sodium chloride (100 mM) and sodium bromide (25 mM), respectively (Merck Suprapur). Absorption spectra agreed with previously reported spectra⁹ for AuCl_4^- and AuBr_4^- .

Stock solutions of iodide (1 mM) were prepared from a 1.00 M solution of sodium iodide (Merck Suprapur) and 1.00 M sodium perchlorate. Solutions were kept in a refrigerator in the dark and were flushed with nitrogen to avoid oxidation. A stock solution of ICl_2^- (8.4 mM) in 1.00 M sodium chloride was prepared by melting ICl (Merck zur Synthese, m.p. 28 °C) on a water bath at 35 °C and transferring a droplet (137.8 mg) to a weighed 100 ml volumetric flask filled with nitrogen-flushed sodium chloride (0.99 M) and hydrochloric acid (10 mM). After transfer, the flask was weighed, wrapped in a foil, placed on a magnetic stirrer at 40 °C, and nitrogen was passed over the solution. After less than 1 h, all ICl had dissolved. For the 1 M chloride concentration used, the predominant species will be ICl_2^- . Hydrolysis is negligible,¹⁰ and the spectrum (see Figure 1), which agreed with literature,¹¹ showed that the solution was stable for several days.

An iodine stock solution (7.32×10^{-4} M) was prepared by dissolution of a weighed amount (55.74 mg) of iodine (Merck doppelt sublimiert, small particles) in 300 ml nitrogen-flushed sodium perchlorate (1.00 M). Nitrogen was passed over the surface, and the flask was wrapped in a foil. After 15 h on a magnetic stirrer, all iodine had dissolved. The spectrum shown in Figure 1 agrees with literature.¹² The solution was stable for several months, if kept in the dark under nitrogen. The I_2Cl^- -solutions used in the kinetic experiments were prepared by mixing 5 ml iodine

stock solution with 100 ml sodium chloride (1.00 M) in a 200 ml volumetric flask (nitrogen-flushed) which was then filled with sodium perchlorate (1.00 M). A slow decrease of the absorbance peak at 243 nm (cf. Figure 1) indicates a slow decomposition during a period of some days. Therefore, all solutions used were freshly prepared.

Apparatus. Spectra were recorded using Cary 14 and Beckman 25 recording spectrophotometers. The stopped-flow instrument was the same as described previously.¹³

Gold(I) Spectra and Equilibria. To 100 ml of a tetrachloroaurate(III) solution ($C_{\text{Au}} = 1 \times 10^{-4}$ M, $C_{\text{NaCl}} = C_{\text{NaClO}_4} = 0.50$ M) was added an equivalent amount of sulphite (2.0 ml 5 mM $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, Merck p.a.). Reduction was complete within one hour. The solution is stable for several hours.² The reduction products are AuCl_2^- and sulphate, but the high chloride concentration is likely to suppress formation of any sulphato complexes. The spectrum of the solution has no absorption bands between 500 and 200 nm. Spectra of solutions having a gold(I) concentration of 4×10^{-6} M (prepared from the solution described above) and iodide concentrations of 0.4, 2, 4 and 6 μM and with sodium chloride (0.50 M) were also recorded. There is an absorption maximum at 223 nm, which increases linearly with the iodide concentration and which has a molar absorptivity (per mole of iodide) of $1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$. Both the position of the band and its molar absorptivity indicate that it is due to free iodide.¹⁴ Thus, complex formation according to eqns. 7 is probably insignificant in these solutions. For larger concentrations of gold(I) (4×10^{-5} M) and iodide (2×10^{-5}) there is an immediate precipitation of AuI(s) .

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Polyhalide Spectra and Equilibria. The spectrum of ICl_2^- shown in Figure 1 was recorded using 8.4×10^{-6} M and 4.2×10^{-3} M solutions containing 1.00 M sodium chloride to displace equilibrium 2 to the right. There is a strong band at 223 nm with a molar absorptivity of $4.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ and a weaker one at 340 nm ($2.6 \times 10^2 \text{ cm}^{-1} \text{ M}^{-1}$). The spectrum agrees rather well with literature.^{11,15} The equilibrium constant $K_2 = [\text{ICl}_2^-]/([\text{ICl}][\text{Cl}^-])$ for reaction 2 was calculated from the absorbance at the 223 nm peak of three solutions with varying chloride concentrations, C_{Cl^-} , (1.00 mM, 11.0 mM, and 1.00 M) and a constant concentration of ICl_2^- , $C_{\text{ICl}_2^-} = [\text{ICl}_2^-] + [\text{ICl}] = 8.4 \times 10^{-6}$ M ($\ll C_{\text{Cl}^-}$). The absorptivities, $\epsilon = \epsilon_{\text{ICl}}[\text{ICl}] + \epsilon_{\text{ICl}_2^-}[\text{ICl}_2^-]$, were 0.026, 0.179, and 0.354 cm^{-1} , respectively, which gave $K_2 = 90 \text{ M}^{-1}$, if $\epsilon_{\text{ICl}} \ll \epsilon_{\text{ICl}_2^-}$, at the wavelength used. There is a previous value for K_2 of $(160 \pm 30) \text{ M}^{-1}$.¹⁶ Hydrolysis of ICl in these solutions is very slow and was suppressed by addition of hydrochloric or perchloric acid (0.100 M).¹⁰ The value of K_2 implies that $[\text{ICl}_2^-] \gg [\text{ICl}]$ for the chloride concentrations used in the kinetics (cf. Tables).

The spectrum of I_2Cl^- and the equilibrium constant for reaction 5 were calculated from the spectra of three solutions, which were mixed from iodine, sodium chloride and sodium perchlorate stock solutions. The total concentration of iodine, $C_{\text{I}_2} = [\text{I}_2] + [\text{I}_2\text{Cl}^-]$ was 2.20×10^{-5} M ($\ll C_{\text{Cl}^-}$) and the chloride concentration C_{Cl^-} was varied (10.0 mM, 100 mM, 1.00 M). From the absorptivities at 243 nm, $\epsilon = \epsilon_{\text{I}_2}[\text{I}_2] + \epsilon_{\text{I}_2\text{Cl}^-}[\text{I}_2\text{Cl}^-]$ (0.015, 0.200, and 0.807 cm^{-1} , respectively), and $\epsilon_{\text{I}_2} = 390 \text{ cm}^{-1} \text{ M}^{-1}$, $K_5 = [\text{I}_2][\text{Cl}^-]/[\text{I}_2\text{Cl}^-]$ was obtained as 0.57 M, in good agreement with literature.⁵ Thus, for the kinetic experiments with 0.50 M chloride (Tables 1 and 3), the concentration ratio is $[\text{I}_2\text{Cl}^-]/[\text{I}_2] = 0.87$. The spectrum of I_2Cl^-

shown in Figure 1 was calculated from the I_2 -spectrum in Figure 1 and the equilibrium constant K_5 . I_2Cl^- has a band at 243 nm with $\epsilon = 2.9 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$. There seems to be agreement in the literature that there is an absorbance maximum between 245 and 250 nm, but the molar absorptivities reported scatter between 1×10^4 and $5.5 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.^{11,17}

The equilibrium constant $K_4 = [I_2Cl^-][Cl^-]/([ICl_2^-][I^-])$ for reaction 4 was calculated by iteration from the absorbance at 243 and 223 nm of a solution with $C_{Cl} = 1.92 \text{ M}$ and $C_{I_2} = 2.9 \times 10^{-6} \text{ M}$ using the known molar absorptivities of I_2Cl^- , ICl_2^- and I^- . $K_4 = 3 \times 10^6$ was obtained in good agreement with K_3/K_2 .

Kinetics. Pseudo first-order rate constants were calculated from experiments with either excess iodide or excess gold(III) complex. For excess iodide (Table 1 and 2) only one reaction could be observed, at all wavelengths, but for excess $AuCl_4^-$, there is one fast increase of absorbance at 260 nm, followed by an equally large slow decrease. The spectra in Figure 1 show that at 260 nm, the molar absorptivities for $AuCl_4^-$ and ICl_2^- are equal, about $10^3 \text{ cm}^{-1} \text{ M}^{-1}$, whereas that of I_2 is negligible. The observed change can therefore be described as a formation of I_2Cl^- in the first step, followed by a disappearance of this species in the subsequent step.

The slow subsequent reaction could be carefully monitored by delaying the start of the oscilloscope sweep until the fast reaction was complete (Table 3, Subsequent reaction). It could also be followed directly by mixing $AuCl_4^-$ solutions with solutions of I_2Cl^- (Table 3, Direct reaction). The chloride system was studied at 25.0 °C only, whereas the much faster $AuBr_4^-$ - iodide reaction was monitored at 3.8, 15.8 and 25.0 °C and 255 nm (Table 2).

In the experiments with excess AuCl_4^- , both solutions mixed in the stopped-flow instrument had the same concentrations of chloride. Thus, there was no shift in the $\text{I}_2\text{Cl}^-/\text{I}_2$ equilibrium 5. In the experiments with excess iodide, one of the drive syringes contained sodium iodide and the other gold(III) complex with chloride or bromide in excess.

The polyhalide reactions 2-6 are fast in the stopped-flow time scale. For instance, the triiodide formation rate constant according to reaction 6 is $4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.¹⁸ Only reaction 4 could be qualitatively followed using second-order conditions and very low initial concentrations ($[\text{I}^-] = [\text{ICl}_2^-] = 2.5 \times 10^{-6} \text{ M}$; $[\text{Cl}^-] = 0.50 \text{ M}$ after mixing). As expected the absorbance decreased at 223 nm and increased at 250 nm, compare Figure 1. The reaction was complete within 100 ms, which means that the rate constant is at least $10^7 \text{ M}^{-1} \text{ s}^{-1}$, if complete conversion to I_2Cl^- is assumed.

Results and Discussion

Stoichiometry. The standard electrode potential for I_2/I^- is 0.615 V for a 0.1 M chloride medium¹⁹ and that for $\text{AuCl}_4^-/\text{AuCl}_2^-$ can be calculated to be 0.926 V from literature data²⁰ for $\text{AuCl}_2^-/\text{Au}$ (1.154 V) and $\text{AuCl}_4^-/\text{Au}$ (1.002 V). For low concentrations of chloride the reduction of AuCl_4^- by iodide can be written

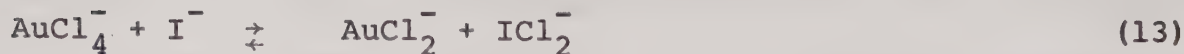


with $E^\circ = 0.311 \text{ V}$ corresponding to $K_{11} = 3 \times 10^{10} \text{ M}$. For larger chloride concentrations, I_2Cl^- will be the main reaction product:



The equilibrium constant for reaction 12 is $K_{12} = K_{11}/K_5 = 3 \times 10^{10}/0.57 = 6 \times 10^{10}$. Thus, for excess iodide, reduction both according to eq. 11 and 12 is complete.

For smaller concentrations of iodide, the main process is:



with $K_{13} = K_{12}/K_4 = 6 \times 10^{10}/(3 \times 10^6) = 2 \times 10^4$. In this case also, reduction is practically complete for the concentrations used. Accordingly, the spectrum between 360 and 260 nm of a solution with $C_{\text{I}} \leq C_{\text{Au}} \approx 1 \times 10^{-5}$ M and $C_{\text{Cl}} = 0.90$ M indicates complete reduction.

In the experiments with excess tetrachloroaurate(III) summarized in Table 3, we must also consider reduction according to eq. 9. The equilibrium constant is $K_9 = K_{13}/K_4 = 2 \times 10^4/(3 \times 10^6) = 1 \times 10^{-2}$, which indicates that in this case also, reduction is complete for the concentrations used. This was confirmed by the spectrum between 350 and 200 nm of a solution with $C_{\text{I}_2} \leq C_{\text{Au}} \approx 1 \times 10^{-5}$ M and $C_{\text{Cl}} = 0.50$ M.

The magnitude of the absorbance changes in the kinetic runs also gives information about the stoichiometry. At 260 nm, the change in absorptivity per molar unit of AuCl_4^- in the experiments with excess iodide, is twice the change per molar unit of iodide observed for the rapid reaction when AuCl_4^- is in excess. This is compatible with a model, where one equivalent of I_2Cl^- per equivalent of AuCl_4^- is formed in the single reaction observed when excess iodide is used according to reaction 8. For excess AuCl_4^- , on the other hand, only half an equivalent of I_2Cl^- is formed per initial mole of iodide in the rapid reaction step, in accordance with reaction 12. The absorbance change for the slow

subsequent step indicates that the I_2Cl^- formed in the rapid step disappears completely in a further reduction according to eq. 9.

Rate Laws, Excess Iodide. For excess iodide, we follow the disappearance of AuCl_4^- and formation of an equilibrium mixture of I_2Cl^- , I_2 and I_3^- according to reactions 1 to 6. The absorbance at 260 nm increases and that at 315 nm decreases, compare spectra in Figure 1. With reaction 1 rate-determining and 2 to 6 rapid, we have the simple rate law:

$$- \frac{d[\text{AuCl}_4^-]}{dt} = k_{r1} [\text{I}^-] [\text{AuCl}_4^-] = k_{\text{exp}} [\text{AuCl}_4^-] \quad (14)$$

Figure 2a shows a plot of the observed rate constant as a function of iodide concentration. The experiments at the two wavelengths agree. The slope of the plot in Figure 2a gives $k_{r1} = (8.5 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. It should be noted that - contrary to the previous report by Hall and Satchell⁸ - the rate is independent of chloride concentration, see Table 1.

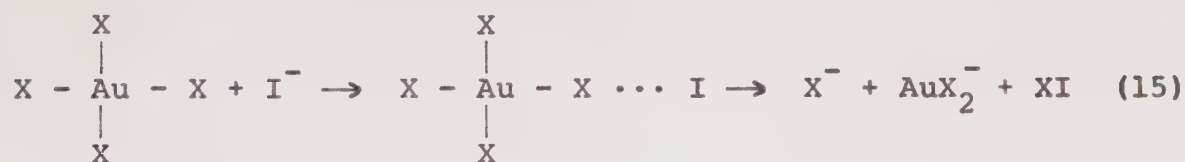
The results for the AuBr_4^- -iodide reaction given in Table 1 also agree with a rate law analogous to eq. 14, but because of the rapid kinetics, the experimental scatter is much larger in this case. Approximate k_{r1} - constants are given in Table 4. The activation energy for the reduction of AuBr_4^- by iodide is approximately $(30 \pm 5) \text{ kJ/mol}$ or $(7 \pm 2) \text{ kcal/mol}$.

Intimate Mechanism for Reduction with Iodide. The spectral changes between 220 and 370 nm for the single reaction observed when excess iodide is used are compatible with a change from AuCl_4^- to I_2Cl^- as the dominant absorbing species, compare the spectra in Figure 1. For instance, isosbestic points can be observed at 235 and 290 nm for this reaction. The over-all process can therefore be written as eq. 8, and a rapid chloride-iodide substitution in

AuCl_4^- followed by a rate-determining reduction can be excluded.

The possibility of a rate-determining ligand substitution followed by a rapid reduction also seems less likely. If we consider the rate constants for the monosubstitution of a chloride in AuCl_4^- by radiochloride ($1.5 \text{ M}^{-1} \text{ s}^{-1}$,²¹), bromide ($63 \text{ M}^{-1} \text{ s}^{-1}$,⁹) and thiocyanate ($1.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$,²²) and of a bromide in AuBr_4^- by chloride ($10.7 \text{ M}^{-1} \text{ s}^{-1}$,⁹) and thiocyanate ($8.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$,²²) and remember that iodide and thiocyanate use to be rather similar as entering ligands, it is not very likely that the rate constants for substitution of a halide by iodide in AuCl_4^- and - especially - in AuBr_4^- are as large as the observed values of $9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

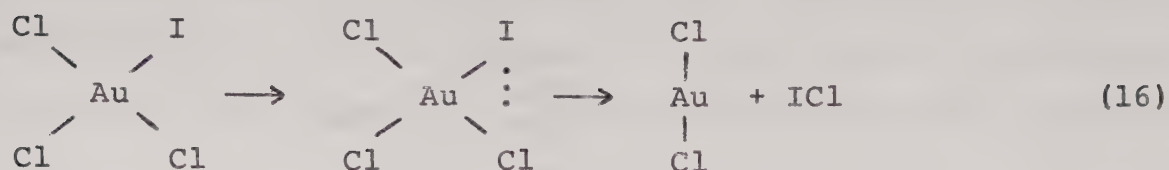
We therefore suggest an intermolecular mechanism, very similar to those used previously to describe square-planar $\longleftrightarrow$ octahedral redox reactions.²³⁻²⁷ Accordingly, there should be a direct attack on the chloride or bromide ligand of the complex by the reducing iodide, without any prior substitution:



According to this model, the difference in rate of reduction by a factor of 100 between the bromide and chloride complex is explained by bromide being a more efficient bridging ligand than chloride.

Pearson²⁸ has discussed an alternative mechanism for linear $\longleftrightarrow$ square-planar redox reactions. Applied to the present process, it should involve a rapid initial ligand substitution, in which AuCl_3I^- is formed according to eq. 10. The reaction proceeds via an E_u -bending motion, so that the halogen molecule ICl is formed

from an iodide and a chloride ligand cis to each other:



This mechanism involves a rather extreme rearrangement of the ligands of the complex. Moreover, the reverse process (i.e. the oxidative cis-addition) has a rather high energy barrier, because one filled d-orbital of the linear complex has its lobe in the I-Cl bond and therefore will be raised in energy.²⁸ Applied to the reductive elimination this means that the E_u -bending involved in eq. 16 must be strongly activated; it is hardly possible for the ground-state AuCl_3I^- to react in this manner. There are no such problems connected with the mechanism according to eq. 15. It should also be noted in this context that the intermolecular mechanism proposed by Ford-Smith and coworkers²⁹ for the oxidation of $\text{Au}(\text{CN})_2^-$ by iodine, which involves oxidative trans-addition, is not symmetry allowed.²⁸ The kinetics for that reaction can also be explained by a mechanism according to the reverse of eq. 15.

Excess Complex, Rapid Reaction. For excess gold and with iodide as the initial reductant, there are two reactions. The increase of absorbance at 260 nm for the rapid initial process corresponds to formation of half an equivalent of $\text{I}_2\text{Cl}^-/\text{I}_2$ equilibrium mixture per mole of iodide originally present. Even for the small concentrations of free iodide used in these experiments (less than 10^{-7} M after reduction, expts. in Table 1), the rapid equilibria according to eq. 2, 3, and 4 are displaced towards the right, whereas formation of I_3^- according to eq. 6 and of ICl_2^- according to eq. 13 will be negligible, compare the

equilibrium constants given previously. The main reaction products will be I_2 and I_2Cl^- according to eq. 11 and 12. Thus, for each equivalent of gold(III) reduced, two equivalents of iodide are consumed. With reaction 1 rate-determining and 2 to 5 rapid, we have

$$-d[I^-]/dt = 2 d([I_2Cl^-] + [I_2])/dt = 2 d[AuCl_4^-]/dt \quad (16)$$

which gives

$$-d[I^-]/dt = 2 k_{r1} [AuCl_4^-][I^-] = k_{exp}[I^-] \quad (17)$$

Figure 2b shows a plot of the experiments in Table 1 according to eq.

17. The scatter is rather large, because the infinity values are disturbed by the subsequent process in these experiments. However, the slope ($2 k_{r1}$) gives $k_{r1} = (9 \pm 2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, which agrees satisfactorily with the value calculated from the experiments using excess iodide cf. Table 4. Thus, the rapid initial process can be interpreted as a reduction of tetrachloroaurate(III) by half of the amount of added iodide.

Excess Complex, Slow Reaction. The slow subsequent process is accompanied by a decrease of the absorbance at 260 nm, equal in magnitude to the initial rapid increase and corresponding to a disappearance of the I_2Cl^-/I_2 equilibrium mixture formed in the rapid step. The experiments both with I^- and I_2Cl^- as initial reductants are summarized in Table . The experimental values show that the reaction is first-order with respect to tetrachloroaurate(III) and that the processes observed when either iodide or I_2Cl^- is used as the initial reductant are identical.

Rate constants were calculated assuming a first-order dependence with respect to I_2Cl^- , compare eq. 9. For excess tetrachloroaurate(III) and chloride we get:

$$-d([I_2Cl^-] + [I_2])/dt = k_{exp}[I_2Cl^-] \quad (18)$$

The variation of the observed rate constant with the concentration of complex and chloride cf. Table 3 can be expressed as

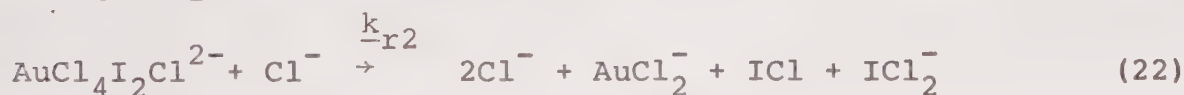
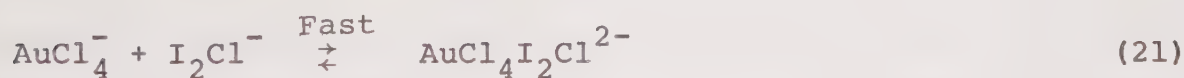
$$k_{exp} = \underline{K}' [Cl^-][AuCl_4^-] / (1 + \underline{K}'' / [Cl^-]) \quad (19)$$

which can be rearranged to the linear relation

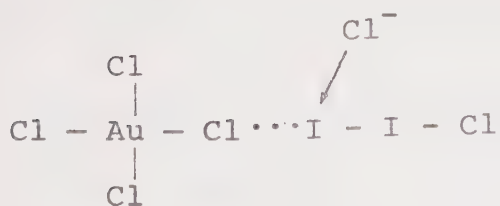
$$[Cl^-][AuCl_4^-]/k_{exp} = 1/\underline{K}' + \underline{K}'' / (\underline{K}' [Cl^-]) \quad (20)$$

The plot in Figure 3 gives $\underline{K}' = (6 \pm 1) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ and $\underline{K}'' = (0.51 \pm 0.05) \text{ M}$.

Mechanism for the Slow Reaction. The value of $\underline{K}''$ obtained from the kinetics agrees rather well with the equilibrium constant $K_5 = 0.57 \text{ M}$, which might indicate that reaction 5 is involved as a fast pre-equilibrium. One possible mechanism compatible with the rate law, eqns. 18 and 19, is a rapid equilibrium according to eq. 5 followed by



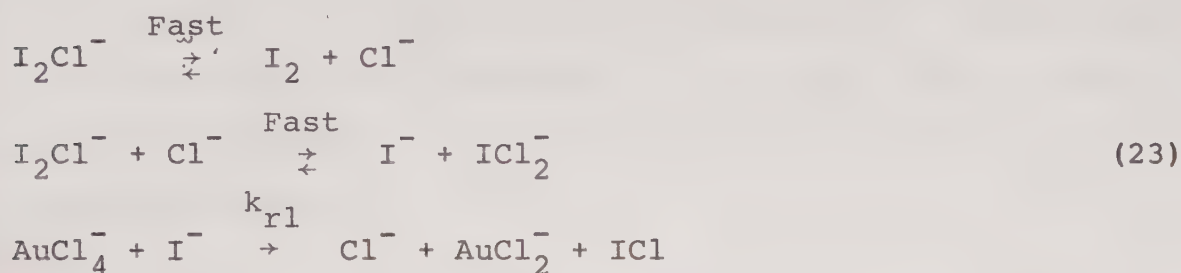
Here, the ion pair formed in the hypothetical rapid equilibrium 21 is reduced in the rate-determining step, eq. 22, for instance via an attack by chloride on one of the iodides of the I_2Cl^- -unit:



In this case, the parameter $\underline{K}'$ of eq. 19 should be identified with

the product $\underline{K}_{21}k_{r2}$. The experimental value, $6 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$, gives no hint as to the probability of this mechanism, since neither $\underline{K}_{21}$ nor k_{r2} are known.

We have also considered the possibility that the rate-determining step for the slow reaction is the same as for the fast one, i.e. a direct reduction of the gold complex by free iodide according to eq. 1. In that case it is necessary to postulate that reaction 5 and the reverse of reaction 4 are involved as rapid pre-equilibria:³⁰



This mechanism leads to the rate expression

$$\frac{d[\text{ICl}_2^-]}{dt} = \frac{\underline{K}_4^{-1} k_{r1} [\text{Cl}^-] [\text{AuCl}_4^-]}{2(1 + \underline{K}_5/[\text{Cl}^-]) [\text{ICl}_2^-] + [\text{Cl}^-]/\underline{K}_4} (\underline{C}_I - [\text{ICl}_2^-]) \quad (24)$$

where $\underline{C}_I$ denotes the total concentration of iodide. In the denominator of eq. 24, $[\text{Cl}^-]/\underline{K}_4$ is small compared to the other term, so the equation might be simplified to

$$d[\text{ICl}_2^-]/dt = \underline{k}' (\underline{C}_I - [\text{ICl}_2^-]) / [\text{ICl}_2^-] \quad (25)$$

where the rate constant $\underline{k}'$ is given by:

$$\underline{k}' = \frac{1}{2} \underline{K}_4^{-1} k_{r1} [\text{Cl}^-] [\text{AuCl}_4^-] / (1 + \underline{K}_5/[\text{Cl}^-]) \quad (26)$$

which agrees with the experimental eq. 19. Integration of eq. 24, however, leads to rate expression 27, which is not strictly

first-order with respect to I_2Cl^- :

$$\ln([\text{ICl}_2^-]_{\text{eq}} - [\text{ICl}_2^-]) = \ln([\text{ICl}_2^-]_{\text{eq}} - [\text{ICl}_2^-]_0) - \frac{t}{\tau} \frac{k'}{[\text{ICl}_2^-]_{\text{eq}}} - ([\text{ICl}_2^-] - [\text{ICl}_2^-]_0)/[\text{ICl}_2^-]_{\text{eq}} \quad (27)$$

For a given experiment k' can be calculated from eq. 26 (using the previously determined value of k_{r1}), and $[\text{ICl}_2^-]_{\text{eq}}$ and $[\text{ICl}_2^-]_0$ are known. Corresponding values of τ and $[\text{ICl}_2^-]$ can then be obtained from eq. 27 by iteration. If the slightly curved plot of the left member of eq. 27 which is then obtained ^{is} approximated by a straight line, and rate constants are calculated from the slope of this line (as in the evaluation of the experiments), the agreement with the experimental rate constants is not better than a factor of about five, however. This does not speak in favour of the reaction mechanism according to eqns. 23.

Finally, in the previous investigation of the AuCl_4^- -iodide reaction by Hall and Satchell,⁸ second-order conditions with equal initial concentrations $[\text{AuCl}_4^-]_0 = [\text{I}^-]_0 = 1 \times 10^{-4} \text{M}$ were used. From the present experiments, we can conclude that half of the amount of gold(III) should be rapidly reduced to gold(I) according to eq. 12 under these experimental conditions, and that the process observed was probably the slow reduction according to eq. 9. The observed rate constant (multiplied by 2 since the initial concentrations were only half of those assumed) should then be described by eqn. 19 with $k' = 6 \times 10^3 \text{M}^{-2} \text{s}^{-1}$ and $k'' = 0.51 \text{M}$. The agreement between the calculated values and those found by H & S is rather good for $[\text{Cl}^-] \geq 0.6 \text{M}$. The deviations are larger (within a factor of 3) for smaller chloride concentrations, probably because of formation of mixed chloro-iodo complexes according to eqns. 7.

To conclude, the present and other^{9,22} experimental studies lend no support for the reaction mechanisms proposed by Hall and Satchell⁸ for substitution reactions in square-planar gold(III) systems.

Acknowledgement. We thank Bodil Jönsson and Ingegerd Lind
for experimental assistance and the Swedish Natural Science
Research Council and the Royal Physiographic Society of Lund
for financial support.

Figure Captions

Figure 1. Spectra of AuCl_4^- , I_2Cl^- , ICl_2^- and I_2 . AuCl_2^- is transparent between 200 and 500 nm.

Figure 2. Reduction of tetrachloroaurate(III) by iodide. (a). Excess iodide. The observed rate constant vs. $\frac{C_{\text{I}}}{C_{\text{Au}}}$. The total concentration of complex was 6.36×10^{-6} M (o) and 3.18×10^{-6} M ($\square$). (b). Excess tetrachloroaurate(III). The observed rate constant for the rapid, initial process vs. $\frac{C_{\text{Au}}}{C_{\text{I}}}$ at 260 nm ($\square$) and 315 nm (o). The total concentration of iodide was 2.5×10^{-6} M.

Figure 3. Plot of $\frac{C_{\text{Cl}} C_{\text{Au}}}{k_{\text{exp}}}$ vs. $1/C_{\text{Cl}}$ for the slow, subsequent process, compare eq. 20. The total concentration of I_2Cl^- was 8.2×10^{-6} (o), 1.13×10^{-5} ($\square$), 1.23×10^{-5} (Δ), and 1.39×10^{-5} M (∇).

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- (30) That reaction 4 is rapid in the time scale of the subsequent, slow reaction follows from the kinetic experiment described in the Experimental Section and the value of K_4 .

Table 1. Observed Rate Constants for Reduction of AuCl_4^- by Iodide at 25.0 °C. The ionic medium was 1.00 M sodium perchlorate and the hydrogen ion concentration was 5×10^{-3} M when not otherwise stated.

$\underline{C}_{\text{Cl}}/\text{M}$	$10^4 \underline{C}_{\text{I}}/\text{M}$	$10^6 \underline{C}_{\text{Au}}/\text{M}$	$\underline{k}_{\text{exp}}/\text{s}^{-1}$ Mean	$\underline{\lambda}/\text{nm}$
<u>Excess Iodide</u>				
0.500	1.19	6.36	8.8	260 or 315
	1.99		16.6	
	2.98		24.0	
	3.97		32.5	
	4.96		41.5	
0.500	1.19	3.18	9.5	260
	1.99		15.4	
	2.98		24.0	
	3.97		32.2	
	4.96		41.6	
0.0100	1.49	6.36	10.5 ^a	260 or 315
0.100	1.49		11.9 ^a	
0.300	1.49		12.1 ^a	
0.850	1.49		12.8 ^a	
<u>Excess Complex, Rapid Reaction</u>				
0.500	0.025	25.4	4.0	315
		50.8	5.6	
		76.0	8.2	
		102	18.5	
		127	14.3	
0.500	0.025	25.4	5.4	260
		50.8	10.0	
		76.2	20.2	
		102	24.2	
		127	30.4	
0.500 ^b	0.0993	127	27.2	260
		254	42.7	
		381	55.6	
		508	63.3	

a. $[\text{H}^+] = 0.1$ M in these expts. in order to suppress hydrolysis of AuCl_4^- .

b. In these four expts., the subsequent process was also monitored, cf. Table 3.

Table 2. Observed Rate Constants for Reduction of AuBr_4^- by Iodide. The total concentrations were $C_{\text{Br}} = 5 \times 10^{-3} \text{ M}$, $[\text{H}^+] = 5 \times 10^{-3} \text{ M}$, $C_{\text{Au}} = 1.27 \times 10^{-6} \text{ M}$ and the wavelength was 255 nm.

$t/^{\circ}\text{C}$	$10^5 C_{\text{I}}/\text{M}$	$k_{\text{exp}}/\text{s}^{-1}$
		Mean
24.9	1.0	82
	1.5	147
	2.0	196
	2.5	214
15.8	1.0	67
	1.5	103
	2.0	157
	2.5	222
	3.0	226
3.8	1.0	58
	1.5	58
	2.0	82
	2.5	114
	3.0	134

Table 3. Observed Rate Constants for the Slow Process at 25.0°C, 260 nm and for a 1.00 Perchlorate Medium.

	$\underline{C}_{Cl}/M$	$10^4 \underline{C}_{Au}/M$	$10k_{exp}/s^{-1}$ Mean
<u>Subsequent reaction</u> ^a	0.50	1.27	2.0
$\underline{C}_{Au} \gg \underline{C}_I = 9.93 \times 10^{-6} M$		2.54	4.1
		3.81	6.0
		5.08	7.6
<u>Direct reaction</u>	0.50	0.95	1.2
$\underline{C}_{Au} \gg \underline{C}_{I_2} = 9.15 \times 10^{-6} M$		1.27	1.5
$\underline{C}_{I_2} = [I_2] + [I_2Cl^-]$		1.90	2.5
$\underline{C}_I = 0$		2.54	3.3
<u>Direct reaction</u>			
$\underline{C}_{I_2} = 1.39 \times 10^{-5} M$	0.130	3.81	0.57
$\underline{C}_{I_2} = 1.23 \times 10^{-5} M$	0.200	2.54	0.94
	0.265	1.91	1.43
	0.500	1.02	1.33
$\underline{C}_{I_2} = 1.13 \times 10^{-5} M$	0.200	2.54	0.79
	0.300	1.65	1.06
	0.500	1.02	1.23
$\underline{C}_{I_2} = 8.2 \times 10^{-6} M$	0.200	2.54	0.84
	0.265	1.91	1.19
	0.500	1.02	1.38
	0.800	0.63	1.90

a. Compare expts. b in Table 1.

Table 4. Rate Constants for Reduction of AuCl_4^- and AuBr_4^- by Iodide in a 1.00 M Sodium Perchlorate Medium.

Complex	$t/^{\circ}\text{C}$	$k_{r1}/\text{M}^{-1}\text{s}^{-1}$	
AuCl_4^-	25.0	$(8.5 \pm 0.3) \times 10^4$	$\underline{C}_{\text{Au}} \ll \underline{C}_{\text{I}}$
		$(9 \pm 2) \times 10^4$	$\underline{C}_{\text{Au}} \gg \underline{C}_{\text{I}}$
AuBr_4^-	3.8	$(4 \pm 2) \times 10^6$	$\underline{C}_{\text{Au}} \ll \underline{C}_{\text{I}}$
	15.8	$(9 \pm 3) \times 10^6$	
	25.0	$(10 \pm 3) \times 10^6$	

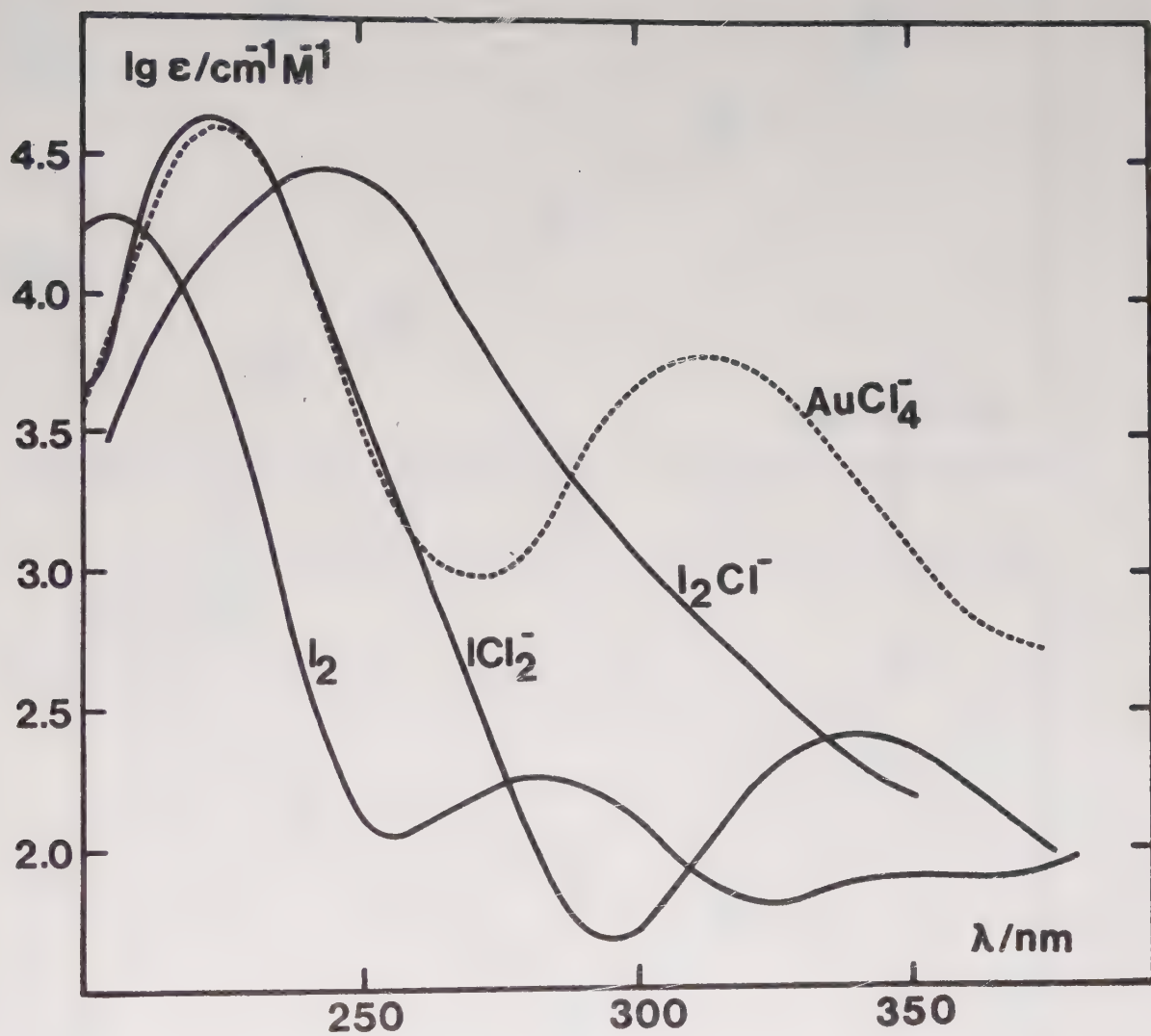


Figure 1. Spectra of AuCl_4^- , I_2Cl^- , ICl_2^- and I_2 . AuCl_2^- is transparent between 200 and 500 nm.

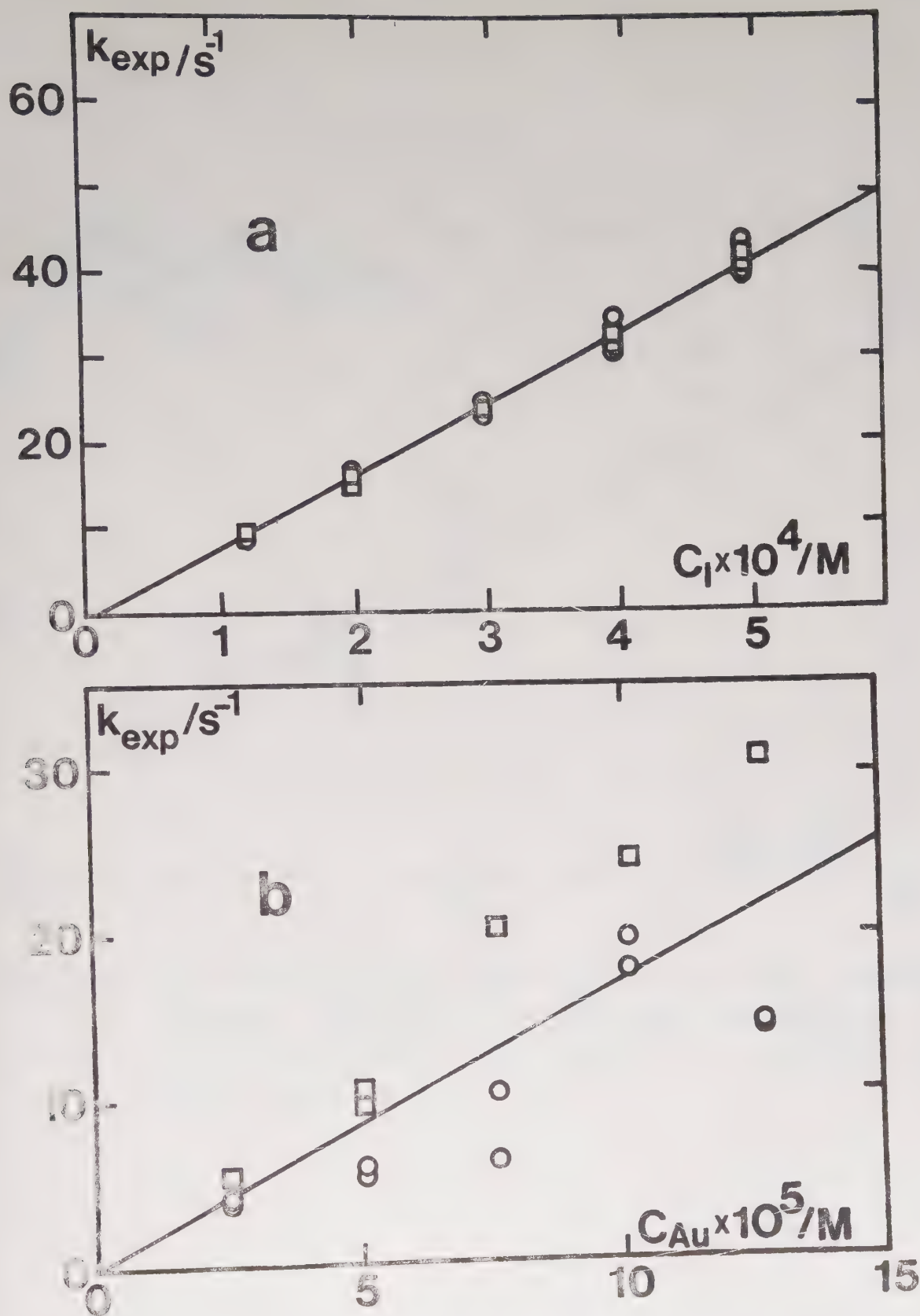


Figure 2. Reduction of tetrachloroaurate(III) by iodide. (a). Excess iodide. The observed rate constant vs. C_I . The total concentration of complex was 6.36×10^{-6} M (o) and 3.18×10^{-6} M ($\square$). (b). Excess tetrachloroaurate(III). The observed rate constant for the rapid, initial process vs. C_{Au} at 260 nm ($\square$) and 315 nm (o). The total concentration of iodide was 2.5×10^{-6} M.

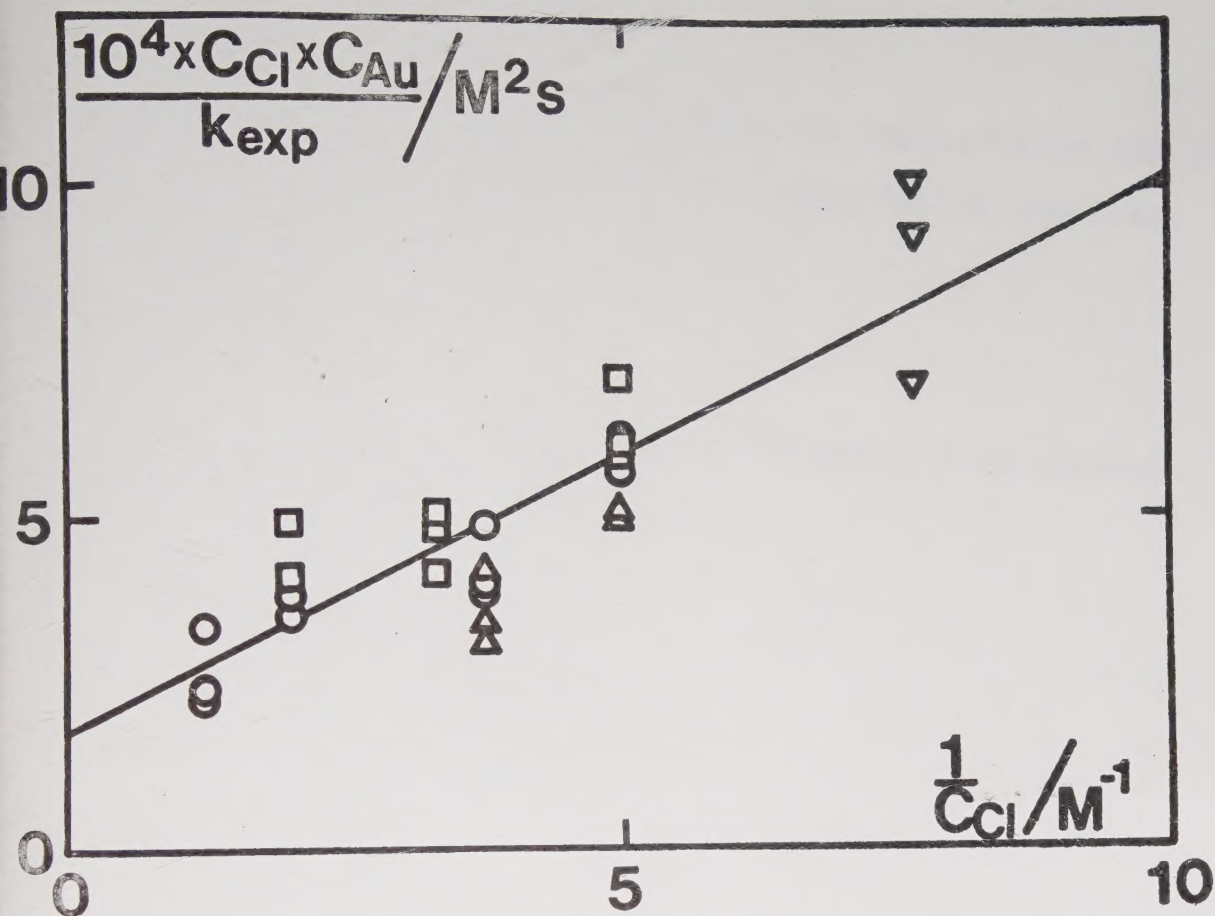


Figure 3. Plot of $\frac{C_{Cl} C_{Au}}{k_{exp}}$ vs. $\frac{1}{C_{Cl}}$ for the slow, subsequent process, compare eq. 20. The total concentration of I_2Cl^- was 8.2×10^{-6} (o), 1.13×10^{-5} (□), 1.23×10^{-5} (Δ), and 1.39×10^{-5} M (▽).

SYMMETRY REQUIREMENTS FOR SUBSTITUTION AND REDOX
PROCESSES OF SQUARE-PLANAR HALIDE COMPLEXES

AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid offentlig
disputation å Kemicentrum, hörsal G, tisdagen den
7 oktober 1980, kl 10.15

av

Lars Fride Olsson

Fil.mag., Kr

